

Solvolyses of naphthoyl chlorides. Solvent effect and Grunwald–Winstein correlation analyses with Y_{xBnCl} scales[†]

Kwang-Ting Liu,* Patty Y.-H. Hwang[‡] and Hun-I Chen

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

Received 21 February 2002; revised 21 June 2002; accepted 5 July 2002

ABSTRACT: The solvolyses of 1-naphthoyl (**2**), 2-naphthoyl (**3**), 4-methyl-1-naphthoyl (**4**) and 6-methoxy-2-naphthoyl (**5**) chlorides in a variety of solvents were studied, and correlation analyses by using the single- and dual-parameter Grunwald–Winstein equations were examined. An excellent linear relationship ($R = 0.995$) for **4**, $\log(k/k_0) = 0.733Y_{\text{xBnCl}} + 0.269N_{\text{OTS}}$, was observed. An $S_{\text{N}}1$ -like mechanism with decreasing extent of nucleophilic solvent participation was found in the solvolysis of **2** and **4**. 2-Naphthoyl chloride is likely to have a mechanism at the borderline of $S_{\text{N}}1$ -like dissociation and an addition–elimination process. 6-Methoxy-2-naphthoyl chloride shows more $S_{\text{N}}1$ -like character than **3** and is associated with nucleophilic solvent intervention more pronounced than that for **2** and **4**. The applicability and the advantages of using the Y_{xBnCl} scale for different types of substrates are discussed. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: naphthoyl chlorides; solvolysis; solvent effect; Grunwald–Winstein correlation analysis

INTRODUCTION

Acyl chlorides are fundamental organic substrates with high reactivity towards many kinds of transformations.¹ Recent examples of physical organic² and synthetic³ studies illustrate continuing interest in research on this category of compounds. Concerning the kinetics and mechanisms of the solvolysis of acyl chlorides, early work by Hudson and co-workers suggested a dependence of the mechanism on solvent composition.⁴ The failure of employing the single-parameter Grunwald–Winstein equation [Eqn. (1)],⁵ with the original Y values, to the solvolysis of 4-nitrobenzoyl chloride⁶ and acetyl and benzoyl chlorides^{4c} in hydroxylic solvents was reported.

$$\log(k/k_0) = mY \quad (1)$$

Mechanistic studies of the solvolysis of benzoyl chlorides have advanced since the 1980s. Bentley *et al.* proposed a limiting $S_{\text{N}}1$ mechanism for the solvolysis of 4-methoxybenzoyl chloride,⁷ and different mechanisms

of solvolysis for aromatic acyl chlorides containing different substituents were suggested from rate–product selectivity studies.⁸ Non-linear $\log k$ vs mY_{Cl} ⁹ plots were observed again.¹⁰ On the other hand, the solvent effect on the solvolytic reactivity of a series of substituted benzoyl chlorides (**1**) was examined^{2c} using the Y values, Y_{BnCl} , derived from the solvolysis rate constants of α -tert-butyl(4-methylphenyl)methyl chloride and 2-aryl-2-chloroadamantane,^{11a,b} specific to benzylic substrates.¹¹ An $S_{\text{N}}1$ mechanism was realized in the case of 2,6-dimethylbenzoyl chloride (**1a**), and $S_{\text{N}}1$ mechanisms with various extents of nucleophilic solvent participation were found in the solvolysis of **1b–d**, while different types of non- $S_{\text{N}}1$ reaction mechanisms were suggested for the parent and deactivated benzoyl chlorides **1e–g**.^{2c} The successful application of the Y_{BnCl} scale to the benzoyl system made it desirable to explore the possibility of employing the Y_{xBnCl} scale, the parameter of solvent ionizing power suitable for the benzylic system with extended charge delocalization based on the use of α -tert-butyl(2-naphthyl)methyl chloride as the reference standard,^{12,13} to the solvolysis of naphthoyl chlorides.

Consequently, the solvolysis of naphthoyl chlorides **2–5** in a variety of solvents was studied. The applicability of the Y_{xBnCl} scale in Grunwald–Winstein-type correlation analyses with single- and dual-parameter equations [Eqns (1) and (2)]¹⁴ can be confirmed, and the mechanism of solvolysis may be understood.

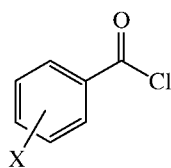
$$\log(k/k_0) = mY + lN \quad (2)$$

*Correspondence to: K.-T. Liu, Department of Chemistry, National Taiwan University, Taipei, Taiwan 106.
E-mail: ktliu@ccms.ntu.edu.tw

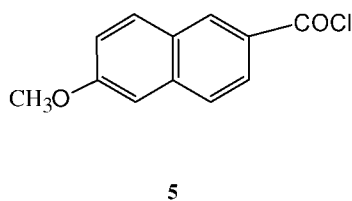
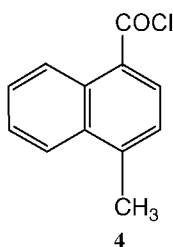
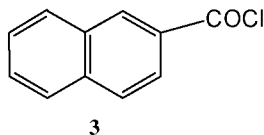
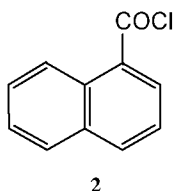
[†]This paper is dedicated to Professor Herbert C. Brown on the occasion of his 90th birthday.

[‡]NSC Undergraduate Research Participant, July 2000 to February 2001.

Contract/grant sponsor: National Science Council, Republic of China.



- 1a** : X = 2,6-(CH₃)₂
1b : X = 2-CH₃
1c : X = 4-CH₃O
1d : X = 4-CH₃
1e : X = 4-H
1f : X = 4-Cl
1g : X = 4-NO₂



RESULTS AND DISCUSSION

1-Naphthoyl chloride (**2**), 2-naphthoyl chloride (**3**), 4-methyl-1-naphthoyl chloride (**4**) and 6-methoxy-2-naphthoyl chloride (**5**) were purified or prepared, and were solvolyzed in a variety of solvents. The rates of

solvolysis were monitored conductometrically at appropriate temperatures. First-order kinetics were observed up to at least 80% of the reaction. The rate constants at 25 °C are shown in Table 1.

The solvolysis of **2** and **3** in acetone–methanol and in acetonitrile–methanol has also been studied by Yoon *et al.*¹⁵ For rate constants of methanolysis, the variation of the two sets of data is within about 10%. Correlation analyses using the single-parameter Grunwald–Winstein equation [Eqn. (1)] against Y_{Cl} ,⁹ Y_{BnCl} ¹¹ and Y_{xBnCl} ¹² were carried out. The results for all solvents (All), nucleophilic solvents (AEM) and iso-dielectric solvents (TE) are listed in Table 2. From this table it is clear that, similarly to those reported previously,^{2c,10} poor correlations and scattered data points for log k – Y_{Cl} plots were found in all four cases.

With the exception of 2-naphthoyl chloride (**3**), in other cases the log k – Y_{xBnCl} plots yielded two lines with excellent correlations ($R \geq 0.99$),¹⁶ one for aqueous acetone, ethanol and methanol (AEM) and the other for the trifluoroethanol–ethanol (TE) mixtures. The log k – Y_{xBnCl} plot for **2** is shown in Fig. 1 as an example. The appearance of a downward splitting line for poorly nucleophilic trifluoroethanol–ethanol mixtures from that for nucleophilic solvents suggests significant nucleophilic solvent intervention in solvolysis, as was illustrated in recent examples.^{2c,17} Moreover, the difference between m_{AEM} and m_{TE} was found to exhibit various extents of nucleophilic solvent intervention.¹⁸ From Table 2, Δm ($m_{\text{AEM}} - m_{\text{TE}}$) of log k – Y_{xBnCl} plots increased from **4** (0.052) to **2** (0.127) to **5** (0.230). Therefore, regression analyses of log k values in Table 1 employing the dual-parameter equation [Eqn. (2)] were carried out. Since the

Table 1. Solvolytic rate constants at 25 °C^a

Solvent ^b	2	3	4	5
100E	2.05×10^{-3}	7.30×10^{-4}	7.00×10^{-3}	7.45×10^{-4}
90E	6.70×10^{-3}	2.08×10^{-3}	2.37×10^{-2}	2.18×10^{-3}
80E	1.69×10^{-2}	3.37×10^{-3}	6.56×10^{-2}	5.46×10^{-3}
70E	4.03×10^{-2}	5.58×10^{-3}	–	1.07×10^{-2}
60E	9.08×10^{-2}	9.33×10^{-3}	–	2.44×10^{-2}
100M	1.51×10^{-2}	4.55×10^{-3}	4.35×10^{-2}	5.40×10^{-3}
90M	2.69×10^{-2}	8.54×10^{-3}	1.52×10^{-1c}	1.29×10^{-2}
80M	9.34×10^{-2}	1.49×10^{-2}	5.13×10^{-1c}	2.60×10^{-3}
70M	3.12×10^{-1c}	2.13×10^{-2}	–	5.97×10^{-2}
90A	5.14×10^{-4}	3.37×10^{-4}	1.10×10^{-3}	–
80A	1.96×10^{-3}	7.58×10^{-4}	5.30×10^{-3}	1.05×10^{-3}
70A	7.21×10^{-3}	1.43×10^{-3}	1.96×10^{-2}	3.16×10^{-3}
60A	2.68×10^{-2}	3.28×10^{-3}	7.81×10^{-2}	9.94×10^{-3}
50A	–	9.24×10^{-3}	–	3.44×10^{-2}
100T	5.36×10^{-1c}	8.96×10^{-3}	–	3.33×10^{-2}
80T20E	1.26×10^{-1}	3.29×10^{-3}	1.02^c	1.59×10^{-2}
60T40E	2.88×10^{-2}	1.13×10^{-3}	1.59×10^{-1c}	4.74×10^{-3}
40T60E	9.63×10^{-3}	7.38×10^{-4}	5.00×10^{-2}	2.24×10^{-3}

^a In s^{–1}.

^b Abbreviations of solvents: A = acetone, E = ethanol, M = methanol, T = 2,2,2-trifluoroethanol. Figures shown are percentages by volume in water; 80T20E indicates T–E 80:20 (v/v) and likewise for 60T40E and 40T60E.

^c Extrapolated from the data at lower temperatures (see text).

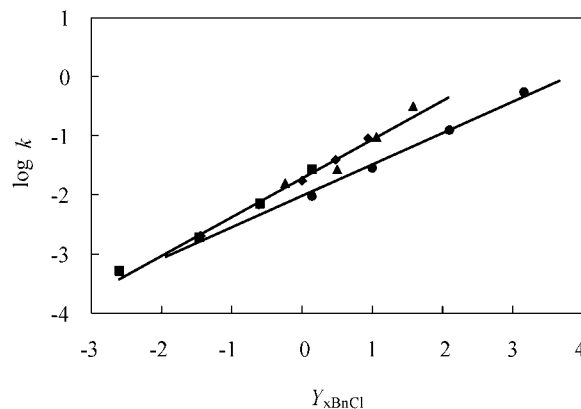
Table 2. Correlation analyses using the single-parameter equation [Eqn. (1)]

Substrate	Parameter	n^a (solvent) ^b	R^c	m (SD) ^d
2	Y_{Cl}	17 (All)	0.968	0.553 (0.037)
		13 (AEM)	0.871	0.531 (0.090)
		5 (TE)	0.990	0.448 (0.037)
	Y_{BnCl}	17 (All)	0.957	0.532 (0.042)
		13 (AEM)	0.987	0.666 (0.033)
		5 (TE)	0.996	0.470 (0.024)
	Y_{xBnCl}	17 (All)	0.968	0.533 (0.036)
		13 (AEM)	0.993	0.657 (0.024)
		5 (TE)	0.997	0.530 (0.025)
3	Y_{Cl}	18 (All)	0.694	0.254 (0.066)
		14 (AEM)	0.794	0.320 (0.071)
		5 (TE)	0.886	0.201 (0.061)
	Y_{BnCl}	18 (All)	0.708	0.260 (0.065)
		14 (AEM)	0.962	0.445 (0.037)
		5 (TE)	0.910	0.215 (0.057)
	Y_{xBnCl}	18 (All)	0.737	0.278 (0.064)
		14 (AEM)	0.982	0.448 (0.025)
		5 (TE)	0.912	0.243 (0.030)
4	Y_{Cl}	13 (All)	0.831	0.653 (0.112)
		10 (AEM)	0.764	0.517 (0.163)
		4 (TE)	0.998	0.620 (0.055)
	Y_{BnCl}	13 (All)	0.970	0.633 (0.048)
		10 (AEM)	0.973	0.720 (0.061)
		4 (TE)	0.999	0.583 (0.016)
	Y_{xBnCl}	13 (All)	0.989	0.650 (0.029)
		10 (AEM)	0.996	0.715 (0.022)
		4 (TE)	0.999	0.663 (0.016)
5	Y_{Cl}	17 (All)	0.846	0.355 (0.058)
		13 (AEM)	0.870	0.414 (0.071)
		5 (TE)	0.992	0.314 (0.023)
	Y_{BnCl}	17 (All)	0.832	0.364 (0.063)
		13 (AEM)	0.994	0.594 (0.020)
		5 (TE)	0.996	0.328 (0.017)
	Y_{xBnCl}	17 (All)	0.842	0.391 (0.065)
		15 (AEM)	0.992	0.600 (0.018)
		5 (TE)	0.996	0.370 (0.066)

^a Number of data points.^b Abbreviations of solvents as in Table 1.^c Correlation coefficient.^d Standard deviation.

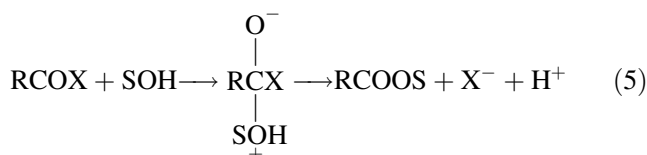
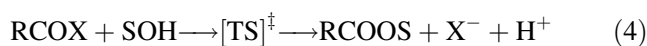
solvent nucleophilicity scale N_{OTs}^{19} was found to be superior to N_T^{20} for substrates bearing anionic leaving groups, such as in the solvolysis of various benzylic¹² and benzoyl chlorides,^{2c} only the former scale was used. A few rate data could not be included owing to the shortage of N values for the corresponding solvents. Nevertheless, it still covers a wide range of both Y (5.76 for Y_{xBnCl}^{12} and 5.83 for Y_{BnCl}^{11}) and N (3.00 for N_{OTs}^{19}) values, and has 11–15 data points, which make the outcome of a dual-parameter regression analysis acceptable. The results are given in Table 3.

Table 3 clearly indicates that an excellent correlation ($R \geq 0.99$)¹⁶ can be found only in the case of **4** if the parameters Y_{xBnCl} and N_{OTs} were applied. A poor correlation ($R < 0.90$) is realized for **3**, whereas the correlations are satisfactory ($R = 0.95$ – 0.98)¹⁶ for **2** and **5** no matter whether the Y_{BnCl} or Y_{xBnCl} scale was

**Figure 1.** Plots of $\log k$ for **2** against Y_{xBnCl} . Data points for (◆) aqueous ethanol (E), (■) aqueous acetone (A), (▲) aqueous methanol (M) and (●) trifluoroethanol–ethanol (TE)

employed. Therefore, the data in Tables 2 and 3 suggest the superiority of using Y_{xBnCl} over other Y values in the correlation analysis for the solvolysis of naphthoyl chlorides.

There are three possible pathways generally considered for the solvolysis of acyl halides, namely the unimolecular S_N1 -type dissociation [Eqn. (3)], the bimolecular synchronous S_N2 -type reaction [Eqn. (4)] and the stepwise addition–elimination reaction [Eqn. (5)], as have been discussed.²¹



Previous work on the mechanism of solvolysis for benzoyl chlorides (**1**) indicated a dependence of the reaction pathways on the nature of the substituents, based on the results of Grunwald–Winstein-type correlation analyses [Eqns (1) and (2)], Hammett-type correlation analysis [Eqn. (6)] and *ab initio* calculations.^{2c} The most reactive and sterically hindered 2,6-dimethylbenzoyl chloride (**1a**) was found to solvolyze with a limiting S_N1 mechanism [Eqn. (3)], whereas the less reactive 2-methyl- (**1b**), 4-methoxy- (**1c**) and 4-methylbenzoyl chloride (**1d**) proceed via an S_N1 mechanism with a significant extent of nucleophilic solvent intervention.^{2c} The unsubstituted benzoyl chloride (**1e**) was considered to solvolyze with a mechanism at the borderline of unimolecular dissociation [Eqn. (3)] and the addition–elimination [Eqn. (5)].^{2c} However, for benzoyl chlorides containing a deactivating substituent, such as 4-chloro- (**1f**) and 4-nitro- (**1g**), an S_N2 -like

Table 3. Correlation analyses using the dual-parameter equation [Eqn. (2)]

Substrate	Parameter	n^a	R	m (SD ^b)	l (SD ^b)
2	$Y_{\text{BnCl}}, N_{\text{OTs}}$	14	0.986	0.656 (0.044)	0.335 (0.069)
	$Y_{\text{xBnCl}}, N_{\text{OTs}}$	14	0.984	0.648 (0.046)	0.241 (0.068)
3	$Y_{\text{BnCl}}, N_{\text{OTs}}$	15	0.850	0.454 (0.082)	0.505 (0.131)
	$Y_{\text{xBnCl}}, N_{\text{OTs}}$	15	0.844	0.454 (0.082)	0.443 (0.125)
4	$Y_{\text{BnCl}}, N_{\text{OTs}}$	11	0.985	0.745 (0.055)	0.432 (0.117)
	$Y_{\text{xBnCl}}, N_{\text{OTs}}$	11	0.995	0.733 (0.031)	0.269 (0.062)
5	$Y_{\text{BnCl}}, N_{\text{OTs}}$	15	0.964	0.587 (0.051)	0.500 (0.081)
	$Y_{\text{xBnCl}}, N_{\text{OTs}}$	15	0.957	0.568 (0.066)	0.403 (0.099)

^a Number of data points.^b Standard deviation.

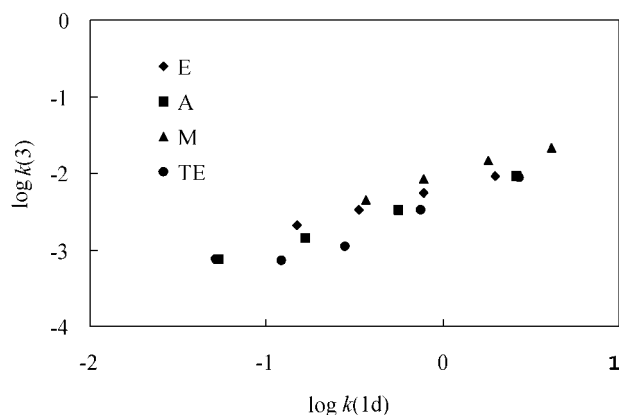
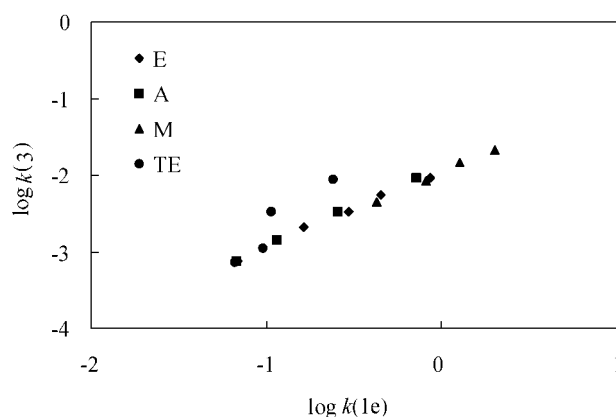
mechanism [Eqn. (4)] was found in nucleophilic solvents and an addition–elimination mechanism [Eqn. (5)] in trifluoroethanol–ethanol.^{2c} Similar variation of mechanisms would be expected to proceed in the solvolysis of naphthoyl chlorides.

$$\log(k_X/k_H) = \sigma^+ \rho \quad (6)$$

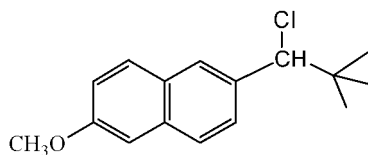
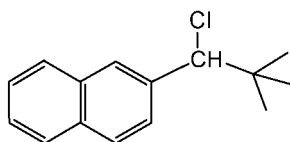
Among the four substrates investigated, 2-naphthoyl chloride (**3**) is the least reactive, as shown from Table 1. A comparison of its rate constants with those for benzoyl chlorides^{2c} indicates that the reactivity lies between those of **1d** and **1e** in the more ionizing solvents, i.e. 70E, 60E, 80M, 70M, 70A to 50A and 100T to 40T60E, in line with the trend of σ^+ constants (−0.311 for CH₃,²² −0.126,²³ −0.135²⁴ or −0.18 (K.-T. Liu, unpublished data) for 2-naphthyl and zero for H). Although the result of correlation analysis using the single-parameter equation [Eqn. (1)] showed similar behavior in nucleophilic solvents for **1d** ($m = 0.662$, $R = 0.990$ against Y_{BnCl})^{2c} and for **3** ($m = 0.448$, $R = 0.982$ against Y_{xBnCl} , Table 2), the correlation was different between **1d** ($R = 0.967$ against Y_{BnCl} and N_{OTs})^{2c} and **3** ($R = 0.844$ against Y_{xBnCl} and N_{OTs} , Table 3) if the rate data in all solvents were considered and Eqn. (2) was used. Logarithmic plots of rate data for **3** in the present study against that for **1d** in

the literature^{2c} also exhibit scattered points (Fig. 2). On the other hand, a poor correlation ($R = 0.924$) was observed for **1e**²⁵ in all solvents by using the dual-parameter equation [Eqn. (2)] against Y_{BnCl} and N_{OTs} . Furthermore, the plot of $\log k(\mathbf{3})$ vs $\log k(\mathbf{1e})$ ^{2c} gave excellent linear relationships ($R = 0.997$) only in aqueous acetone, ethanol and methanol (Fig. 3), and showed significant deviations in 100T and 80T20E. Therefore, the solvolysis mechanism of **3** in nucleophilic solvents might be close to that of benzoyl chloride (**1e**), at the borderline of unimolecular dissociation [Eqn. (3)] and the addition–elimination process [Eqn. (5)], as was suggested.^{2c} The observed acceleration of solvolysis rates for **3** compared with **1e** in weakly nucleophilic solvents (100T and 80T20E, Fig. 3) indicates that the mechanism is closer to the unimolecular dissociation in the case of **3** than **1e**.

Table 1 indicates that 6-methoxy-2-naphthoyl chloride (**5**) is slightly more reactive than the unsubstituted substrate **3** with a rate ratios $k(\mathbf{5})/k(\mathbf{3})$ of 1.3–4.8. However, large rate enhancements, 100–1000-fold, due to increasing resonance stabilization in the cationic transition state by the 6-methoxy group, were found in the solvolysis of the corresponding α -*tert*-butyl(6-methoxy-2-naphthyl)methyl chloride (**6**)²⁶ versus the parent α -*tert*-butyl(2-naphthyl)methyl chloride (**7**).¹² The σ^+

**Figure 2.** Plots of $\log k$ for **3** against $\log k$ for **1d**. Symbols as in Fig. 1**Figure 3.** Plots of $\log k$ for **3** against $\log k$ for **1e**. Symbols as in Fig. 1

constant for the 6-methoxy-2-naphthyl group was estimated as -0.57 (K.-T. Liu, unpublished data). Probably **5** solvolyzed with a mechanism different from that for **3**, but similar to that for **1c** and **1d**. Although no good linear relationship was observed for **5** in the dual-parameter correlation analysis (Table 3), two separate lines, one for nucleophilic solvents (AEM) and the other for poorly nucleophilic solvents (TE), were found in the single-parameter plots (Table 2, Figure 4). Therefore, the downward splitting of line for data points obtained in TE ($m = 0.370$) from that in AEM ($m = 0.600$), i.e. $\Delta m = 0.230$, suggests the intervention of nucleophilic solvents in the ionization process of **5** (see above). The low m values (≤ 0.6) in Tables 2 and 3 obtained from both single-parameter [Eqn. (1)] and dual-parameter [Eqn. (2)] regression analyses also revealed deviations from an S_N1 process. The observation of an excellent linear $\log k(\mathbf{5})$ – $\log k(\mathbf{1d})$ plot with $R = 0.994$ and $m = 0.933$ (Figure 5), but a poor correlation for the $\log k(\mathbf{5})$ – $\log k(\mathbf{1e})$ plot (Fig. 6), provides additional evidence for the similarity of solvolytic mechanisms between **5** and **1d**.

**6****7**

A comparison of $k(\mathbf{2})$ and $k(\mathbf{3})$ (Table 1) reveals that 1-naphthyl chloride (**2**) is more reactive than 2-naphthyl chloride (**3**) in all solvents employed. The rate ratios are

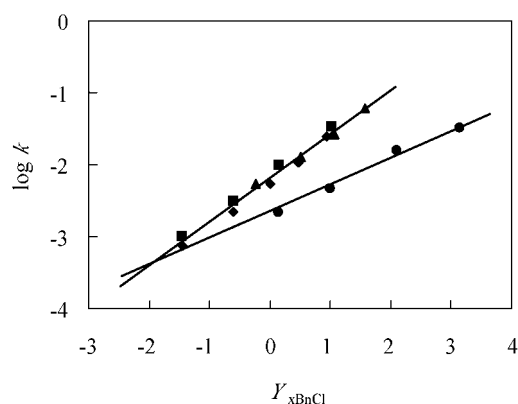


Figure 4. Plots of $\log k$ for **5** against Y_{xBnCl} . Symbols as in Fig. 1

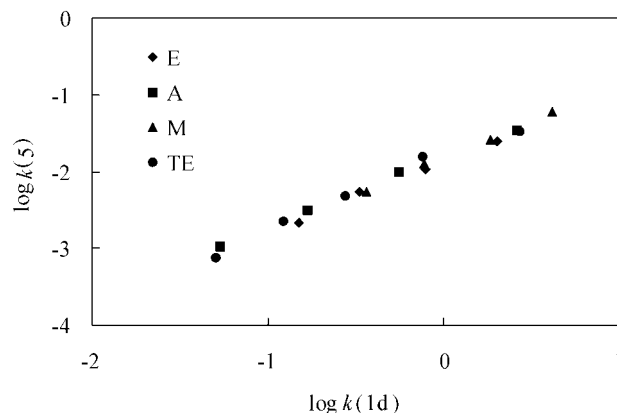


Figure 5. Plots of $\log k$ for **5** against $\log k$ for **1d**. Symbols as in Fig. 1

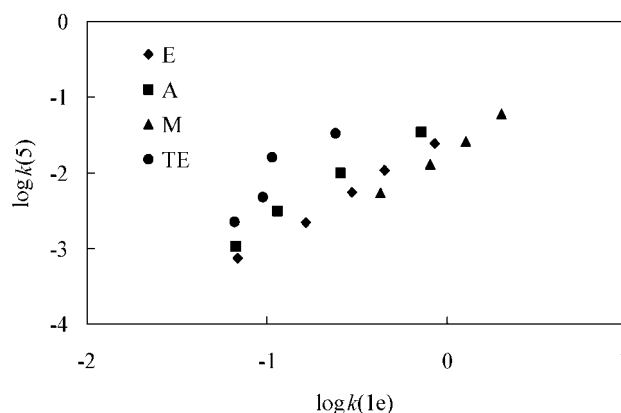
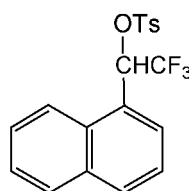
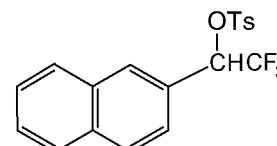


Figure 6. Plots of $\log k$ for **5** against $\log k$ for **1e**. Symbols as in Figure 1

1.5–5.0 in less ionizing but more nucleophilic solvents, about 10–15 in others, and the largest (ca 60) in the least nucleophilic trifluoroethanol. On the other hand, the solvolysis of secondary 1-naphthylmethyl tosylate (**8**) was found to be about 10–25-fold more reactive than the 2-naphthylmethyl analogue **9** in a variety of solvents.²⁷ Both **2** and **3** could therefore be proposed to solvolyze, at least in part, via an ionization mechanism [Eqn. (3)] in solvents such as 60E, 70M, 100T and some other TE mixtures. Indeed, Fig. 1 exhibits a splitting of lines, and

**8****9**

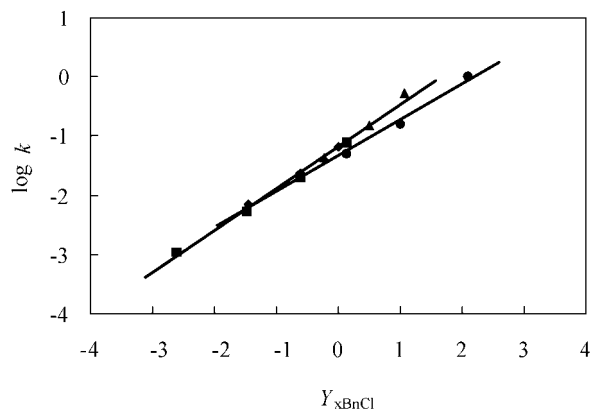


Figure 7. Plots of $\log k$ for **4** against Y_{XBnCl} . Symbols as in Fig. 1

Table 3 shows a fairly good linear relationship ($R=0.984$) from the dual-parameter correlation with Y_{XBnCl} and N_{OTs} in the case of **2**. In other words, **2** is likely to solvolyze via S_N1 mechanisms involving a certain extent of nucleophilic solvent intervention, although it could be partially hindered by the *peri*-hydrogen at C-8.

Table 1 shows a small increment of the solvolytic reactivity, 2–8, for 4-methyl-1-naphthoyl chloride (**4**) over that for 1-naphthoyl chloride (**2**). The $\log k$ – Y_{XBnCl} plot gave two lines in both cases (Figs 1 and 7), and Table 2 reveals a smaller difference in the slopes for **4** ($m_{AEM} - m_{TE} = 0.052$) than that for **2** (0.127). Obviously, the introduction of a 4-methyl substituent gives rise to increased stability of the cationic intermediate, probably due to a resonance effect (**10**) (Scheme 1), and thus a decreased extent of nucleophilic solvent intervention in solvolysis. Since good to excellent linear relationships in the dual-parameter correlation [Eqn. (2)] were observed for **4** ($R=0.995$) and **2** ($R=0.984$), and the N_{OTs} scale was defined from the reaction of methyl tosylate,¹⁷ the intervention of nucleophilic solvents in this study would probably be a kind of ‘participation’²⁸ but not ‘nucleophilic solvation.’²⁹ A discussion on the criteria for nucleophilic solvent participation will be reported elsewhere.

Accordingly, a spectrum of the change in solvolytic mechanisms for the four naphthoyl chlorides **2–5** could

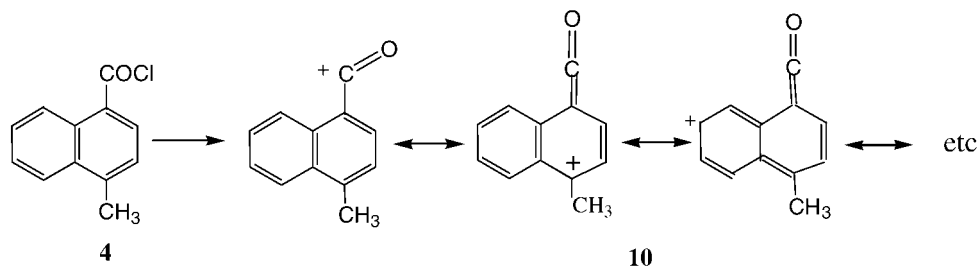
be suggested. The least reactive 2-naphthoyl chloride (**3**) is likely to have a mechanism at the borderline of unimolecular dissociation [Eqn. (3)] and the addition–elimination process [Eqn. (5)]. The more reactive 6-methoxy-2-naphthoyl chloride (**5**) shows more S_N1 -like character but is associated with significant nucleophilic solvent participation. Similarly to **5**, S_N1 -like mechanisms are involved for 1-naphthoyl chloride (**2**) and the most reactive 4-methyl-1-naphthoyl chloride (**4**) and with decreasing extent of nucleophilic solvent participation from **5** to **2** to **4**, in line with the observed Δm ($m_{AEM} - m_{TE}$) of $\log k$ – Y_{XBnCl} plots discussed previously.

Furthermore, the present results demonstrate a further example that the observation of excellent linear correlations in the Grunwald–Winstein-type correlation analysis using the Y_{XBnCl} scale [Eqn. (1)] and Y_{XBnCl} and N_{OTs} scales [Eqn. (2)] as solvent parameters could be regarded as a criterion for the elucidation of solvolysis mechanisms for naphthoyl chlorides **2–5**, in addition to other systems already reported, such as benzhydryl,^{12,13b,c} 9-fluorenyl^{12,13a,30} and *N,N*-diphenylcarbamoyl.^{11c} Although Kevill and co-workers proposed the use of the aromatic ring parameter I together with Y_X and N_T scales [Eqn. (7)] for studying the solvolytic behavior of benzylic substrates,³¹ its inferiority compared with Y_{BnX} for the solvolysis of benzylic³² and benzoyl^{2c,17a} derivatives has already been shown in our previous work. Utilization of Y_{XBnX} was also found to be superior to I and Y_X in benzhydryl and 9-fluorenyl solvolyses.^{12,13,27,33} It is therefore desirable to compare these two approaches in the solvolysis of naphthoyl chlorides. A regression analysis using Eqn. (7), for example, yielded less satisfactory results for **2** [$n=15$ and $R=0.955$, Eqn. (8)] and **4** [$n=12$ and $R=0.981$, Eqn. (9)] than those listed in Table 3. The small magnitudes of h and their large difference (0.767 vs 1.26) also seem to be unreasonable for interpreting the contribution of the naphthalene ring.

$$\log(k/k_0) = mY + lN + hI \quad (7)$$

$$\log(k/k_0) = 0.558 Y_{Cl} + 0.670 N_T + 0.767I \quad (8)$$

$$\log(k/k_0) = 0.697 Y_{Cl} + 0.636 N_T + 1.26I \quad (9)$$



Scheme 1

CONCLUSION

From single- and dual-parameter Grunwald–Winstein-type correlation analyses with Y_{xBnCl} , or Y_{xBnCl} and N_{OTs} scales, the solvolytic mechanisms for naphthoyl chlorides **2–5** could be deduced. Along with the increasing trend of reactivity from **3** to **5** to **2** and to **4**, the mechanism changes from that at the borderline of $S_{\text{N}}1$ -like unimolecular dissociation [Eqn. (3)] and the addition–elimination process [Eqn. (5)] for **3**, to a more $S_{\text{N}}1$ -like route and involving significant nucleophilic solvent intervention for **5**. A purely unimolecular process is associated with a decreasing extent of such a participation for **2–4**. Substituent effects enhancing resonance stabilization of the cationic transition state might be responsible for the increasing reactivity and the changing mechanisms. The present results also demonstrate the wide applicability and the advantage of using the Y_{xBnCl} scale to elucidate the mechanism of solvolysis for different types of substrates.

EXPERIMENTAL

Spectra. Proton and carbon-13 NMR spectra were recorded on a Bruker Model DMX-300 instrument. IR spectra were measured on a Nicolet MANGA-IR 550 spectrometer.

Materials. Spectral-grade or reagent-grade solvents (Merck) were purified following conventional methods³⁴ for kinetic studies. Doubly deionized water was used to prepare aqueous solvent mixtures for solvolytic studies. Commercially available naphthoyl chlorides (**2** and **3**) were purchased from TCI. 4-Methyl-1-naphthoyl chloride (**4**) was synthesized from 1-bromo-4-methylnaphthalene (Aldrich) to 4-methylnaphthalene-1-carboxylic acid³⁵ and then by treating with thionyl chloride.³⁶ 6-Methoxy-2-naphthoyl chloride (**5**) was prepared from the corresponding acid (Aldrich) and thionyl chloride.³⁷ The IR and NMR spectra were found to be in accord with the assigned structures. All chlorides were freshly purified prior to kinetic measurements.

Kinetic measurements. Rate constants were measured by a conductimetric method at least in duplicate. The conductivity cells containing solution of about 1×10^{-4} – 1×10^{-5} M were placed in a thermostat with a temperature variation of $\pm 0.02^\circ\text{C}$. The error for the measurement of k was $\pm 3\%$.

Most of the rate constants were monitored at 25°C . For those measured at low temperatures the values are as follows (in s^{-1}): for **2** in 100T $k(-10^\circ\text{C}) = 2.53 \times 10^{-2}$, $k(-5^\circ\text{C}) = 3.44 \times 10^{-2}$ and $k(0^\circ\text{C}) = 6.70 \times 10^{-2}$, and in 70M $k(-5^\circ\text{C}) = 9.58 \times 10^{-3}$, $k(0^\circ\text{C}) = 1.79 \times 10^{-2}$ and $k(5^\circ\text{C}) = 3.33 \times 10^{-2}$; for **4** in 90M $k(-10^\circ\text{C}) = 3.46 \times 10^{-3}$, $k(-5^\circ\text{C}) = 6.30 \times 10^{-3}$ and

$k(0^\circ\text{C}) = 1.15 \times 10^{-2}$, in 80M, $k(-10^\circ\text{C}) = 1.41 \times 10^{-2}$, $k(-5^\circ\text{C}) = 2.81 \times 10^{-2}$ and $k(0^\circ\text{C}) = 4.26 \times 10^{-2}$, in 80T20E $k(-10^\circ\text{C}) = 2.58 \times 10^{-2}$, $k(-5^\circ\text{C}) = 4.19 \times 10^{-2}$ and $k(0^\circ\text{C}) = 8.20 \times 10^{-2}$, and in 60T40E $k(-5^\circ\text{C}) = 8.20 \times 10^{-3}$, $k(0^\circ\text{C}) = 1.47 \times 10^{-2}$ and $k(5^\circ\text{C}) = 2.35 \times 10^{-2}$. These data were extrapolated to 25°C by the use of an Arrhenius plot. The results at 25°C are summarized in Table 1.

Acknowledgements

We are indebted to the National Science Council, Republic of China, for financial support of this research.

REFERENCES

- (a) Patai S (ed). *The Chemistry of Acyl Halides*. Wiley: Chichester, 1972; (b) Patai S (ed). *The Chemistry of Acid Derivatives, Supplements B*, vol. 2. Wiley: Chichester, 1992; (c) Katrizky AR, Meth-Cohn O, Rees CW (eds). *Comprehensive Organic Functional Groups Transformations*, vol. 5. Elsevier Science: Oxford, 1995, Section 5.01.
- (a) Chao I, Chen K-W, Hwang T-S, Liu K-T. *J. Phys. Org. Chem.* 2001; **14**: 591; (b) Garcia-Riu L, Leis JR. *Chem. Commun.* 2000; 455; (c) Liu K-T, Chen H-I. *J. Chem. Soc., Perkin Trans. 2* 2000; 893; (d) Koo IS, Kim J-S, An SK, Yang K, Lee I. *J. Korean Chem. Soc.* 1999; **43**: 527; *Chem. Abstr.* 2000; **132**: 107619e; (e) Koo IS, Lee SI, An SK, Yang K, Lee I. *Bull. Korean Chem. Soc.* 1999; **20**: 1451; *Chem. Abstr.* 2000; **132**: 236663p.
- (a) Kodomari M, Nagaoka T, Furusawa Y. *Tetrahedron Lett.* 2001; **42**: 3105; (b) Kabalka GW, Malladi RR, Tejedor D, Kelley S. *Tetrahedron Lett.* 2000; **41**: 1001.
- (a) Hudson RF, Wardill JE. *J. Chem. Soc.* 1950; 1729; (b) Hudson RF, Archer BJ. *J. Chem. Soc.* 1950; 3259; (c) Hudson RF, Brown DA. *J. Chem. Soc.* 1953; 883.
- Grunwald E, Winstein S. *J. Am. Chem. Soc.* 1948; **70**: 846.
- Swain CG, Mosely RB. *J. Am. Chem. Soc.* 1955; **77**: 3727.
- Bentley TW, Koo IS, Norman SJ. *J. Org. Chem.* 1991; **56**: 1604.
- (a) Bentley TW, Carter GE, Harris HC. *J. Chem. Soc., Perkin Trans. 2* 1985; 983; (b) Bentley TW, Koo IS. *J. Chem. Soc., Perkin Trans. 2* 1989; 1385; (c) Bentley TW, Shim CS. *J. Chem. Soc., Perkin Trans. 2* 1993; 1659; (d) Bentley TW, Shim CS. *J. Chem. Soc., Perkin Trans. 2* 1993; 2351.
- Bentley TW, Llewellyn G. *Prog. Phys. Org. Chem.* 1990; **17**: 121.
- Bentley TW, Harris HC. *J. Chem. Soc., Perkin Trans. 2* 1986; 619.
- (a) Liu K-T, Sheu H-C. *J. Org. Chem.* 1991; **56**: 3021; (b) Liu K-T, Chang L-W, Yu D-G, Chen P-S, Fan J-D. *J. Phys. Org. Chem.* 1997; **10**: 879; (c) Liu K-T, Chen H-I, Lin Y-S, Jin B-Y. *J. Phys. Org. Chem.* 2000; **13**: 322.
- Liu K-T, Lin Y-S, Tsao M-L. *J. Phys. Org. Chem.* 1998; **11**: 223.
- (a) Liu K-T, Lin Y-S, Tsao M-L. *Org. React.* 1997; **31**: 59; (b) Liu K-T, Chuang C-S. *J. Chin. Chem. Soc.* 2001; **48**: 1047; (c) Liu K-T, Chuang C-S, Jin B-Y. *J. Phys. Org. Chem.* 2002; **14**: 21.
- Winstein S, Grunwald E, Jones HW. *J. Am. Chem. Soc.* 1951; **73**: 2700.
- Yoon SK, Uhm TS, Sung DD. *J. Korean Chem. Soc.* 1980; **24**: 347.
- Jaffe HH. *Chem. Rev.* 1953; **53**: 191.
- (a) Liu K-T, Hou I-J. *Tetrahedron* 2001; **57**: 2343; (b) Liu K-T, Duann Y-F, Hou S-J. *J. Chem. Soc., Perkin Trans. 2* 1998; 2181; (c) Bentley TW, Llewellyn G, Ryu ZH. *J. Org. Chem.* 1998; **63**: 4654.
- Liu K-T, Chen P-S. *J. Chem. Res. (S)* 1994; 310.
- Fujio M, Susuki T, Goto M, Tsuji Y, Yatsugi K, Saeki Y, Kim SH, Tsuno Y. *Bull. Chem. Soc. Jpn.* 1994; **67**: 2233.
- Kevill DN, Anderson SW. *J. Org. Chem.* 1991; **56**: 1845.
- Kivinen A. In *The Chemistry of Acyl Halides*, Patai S (ed). Wiley: Chichester, 1972; 177–230.
- Hansch C, Leo A, Taft RW. *Chem. Rev.* 1991; **91**: 165.

23. Allen AD, Girdhar R, Jansen MP, Mayo JD, Tidwell TT. *J. Org. Chem.* 1986; **51**: 1324.
24. Tsuji Y, Fujio M, Tsuno Y. *Bull. Chem. Soc. Jpn.* 1990; **63**: 856.
25. Chen H-I. PhD Thesis, National Taiwan University, 1999, Chapt. 3.
26. Lin Y-S. PhD Thesis, National Taiwan University, 1997, Chapt. 3.
27. Liu K-T, Hsu H-Y, Yang J-S. *Tetrahedron Lett.* 1992; **33**: 3327.
28. Bentley TW, Bowen CT, Parker W, Watt CIF. *J. Am. Chem. Soc.* 1979; **101**: 2486.
29. Richard JP, Toteva MM, Amyes TL. *Org. Lett.* 2001; **3**: 2225.
30. Liu K-T, Lin Y-S. *J. Chin. Chem. Soc.* 2000; **47**: 71.
31. (a) Kevill DN, Ismail NHJ, D'Souza MJ. *J. Org. Chem.* 1994; **59**: 6303; (b) Kevill DN, D'Souza MJ. *J. Chem. Soc., Perkin Trans. 2* 1995; 973.
32. Liu K-T. *J. Chem. Soc., Perkin Trans. 2* 1996; 327.
33. Liu K-T, Lin Y-S. *Tetrahedron Lett.* 1997; **38**: 1419.
34. Armarego WLF, Perrin DD. *Purification of Laboratory Chemicals* (4th edn). Butterworth-Heinemann: London, 1996.
35. Blatt AH (ed). *Org. Synth., Coll. Vol.* 1943; **2**: 425.
36. Eissenstat MA, Bell MR, D'Ambra TE, Alexander EJ, Daum SJ. *J. Med. Chem.* 1995; **38**: 3094.
37. (a) Fries K, Schimmelschmidt K. *Chem. Ber.* 1925; **58B**: 2835; (b) Leigh WJ, Frendo DT, Klawunn PJ. *Can. J. Chem.* 1985; **63**: 2131.